Fabrication of Few Layer Graphene/ZrO_2 composite powders

A thesis submitted in the partial fulfilment of the requirements

for the degree of Bachelor of Technology

By

Shreeram Jyoti Dash

109CR0109

Supervisor:

Dr. Shantanu Behera

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

CERTIFICATE

This is to certify that the thesis entitled, "Fabrication of FLG/ZrO_2 composite powders" submitted by **Mr. Shreeram Jyoti Dash (109CR0109)** in partial fulfilments for the requirements for the award of Bachelor of Technology degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in this thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

Date: 13/05/2013

Dr. Shantanu Behera

Assistant Professor

Department of Ceramic Engineering

National Institute of Technology

Rourkela – 769008

ACKNOWLEDGEMENT

I express my sincere gratitude to my advisor Dr. Shantanu Behera, National Institute of Technology, Rourkela for his inspiration and guidance and valuable suggestion throughout this research work. It would have been impossible on my part to come out with this project report without him.

I would like to express my gratitude to Dr. Swadesh Kumar Pratihar, HOD, Ceramic Engineering and all other faculties for constant support and valuable suggestions. I would also take this opportunity to express my gratitude to the non-teaching staff for their help and kind support. I am also thankful to the Research Scholars especially Swarnima Kashyap, Geeta Didi, Sanjay Swain and Ganesh Bhai in the Department of Ceramic Engineering for helping out in labs and analysis.

And lastly I am thankful to my friends and my family who encouraged and helped me during the total period of time. Without their support my project would not have been the same.

Shreeram Jyoti Dash

109CR0109

ABSTRACT

Graphene, a monolayer form of carbon with two dimensional honeycomb lattices (sp^2 hybridization) has shown excellent mechanical, electrical, thermal and optical properties. It is a promising component for many applications in the fields of electronics, composites, sensors as well as energy storage and conversion. As a derivative of graphene, graphene oxide has also become an attractive material and been investigated widely in many areas since the ease of synthesizing graphene oxide and its solution processability. Among many other factors, pH of the medium, size of the graphene oxide sheets, etc. are some of the important parameters which makes the graphene dispersible in the medium, detailed study of which is absent in literature. The present work focuses on studying the effect of the pH on the stabilization and dispersability of GO in a polar solvent i.e. water. In this paper, we prepared graphene oxide by the modified Hummers method. The hydrophilicity of graphene oxide with different pH values was characterized with adsorbance in UV-Visible range. Chemically converted graphene was prepared by partial reduction of GO. Few Layer Graphene/zirconia nanocomposites were fabricated by wet chemical method. Such a composite is desired where a percolating network of graphene in the ZrO_2 matrix can increase the electrical conductivity of the composite, while retaining the functional property of the ceramic phase (ZrO_2 in this case). An interesting result was observed. The crystallization of zirconia was delayed, to about 900 ^oC, which is 200-300 ^oC higher than the same prepared from comparable chemical methods in absence of graphene or graphene oxide. Various characterization techniques including SEM, FTIR-spectroscopy, XRD, UV-Vis spectroscopy were used to study the quality of graphene oxide, CCG and FLG – zirconia composites.

LIST OF FIGURES

LIST OF ABBREVIATIONS

Sl no	Abbreviation	Full Form
1	TEM	Transmission Electron Microscopy
2	GO	Graphite Oxide
3	SEM	Scanning Electron Microscopy
4	XRD	X-Ray Diffraction
5	FTIR	Fourier Transform InfraRed
6	AFM	Atomic Force Microscope
7	NMR	Nuclear Magnetic Resonance
8	XPS	X-ray Photoelectron Spectroscopy
9	FLG	Few Layer Graphene
10	SLG	Single Layer Graphene
11	CNT	Carbon Nano Tube
12	MWNT	Multi Wall carbon Nano Tube
13	DI	De-Ionized

CONTENTS

CHAPTER 1

INTRODUCTION

1.1 Graphene:

Graphene, a monolayer form of carbon, is a 2D material arranged in a chicken wire or honeycomb structure as shown in fig 1. The honeycomb lattice is composed of two similar sub-lattices of carbon atoms bonded to each other with σ bonds. Each carbon atom in the honeycomb lattice possesses a π orbital that is mainly responsible for a delocalized network of electrons.

Even though it was considered to be highly unstable in its ground state, the opposite was proved when it was successfully isolated by physicists Andre Geim and Kostya Novoselov at the University of Manchester in 2003 which fetched them Novel Prize later in 2010. With the help of micromechanical cleavage or simply "scotch-tape" method [1], they were able to segregate and pull out single layers of graphene and transferred them onto a thin silica substrate.

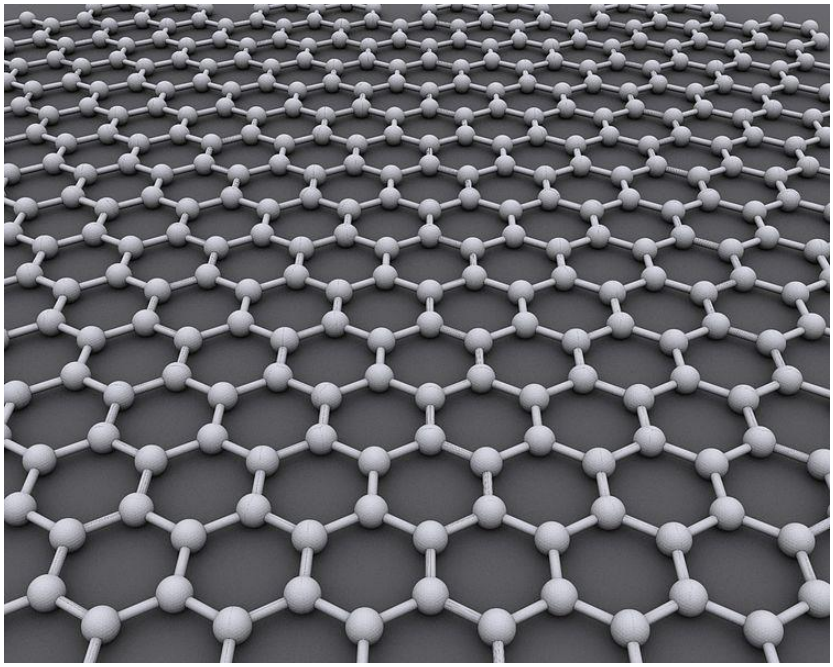


Fig 1. Monolayer structure of Graphene[#]

Graphene, even though the thinnest material known to the scientific community, has shown many interesting properties from the electrical, mechanical, optical and thermal point of view. It has an electrical conductivity similar to that of copper and has the highest thermal conductivity among the materials known to us. Graphene is almost transparent and highly dense at the same time thus not allowing the smallest atom helium to pass through it. These properties have made graphene a material of interest for numerous applications like in the fields of composites, sensors, electronics as well as energy storage and conversion.

A few properties of graphene which makes it special are [2, 3-5]:

- Large theoretical specific area (2360 m2/g)
- Extremely high Young's modulus (~1.0 TPa)
- It is the purest form of carbon
- Optical transmittance (~97.7%)
- High intrinsic mobility (200,000 cm2v−1s−1)
- Thermal conductivity (~5000Wm−1K−1)

1.2 Applications:

- Ultracapacitors
- Frequency Multiplier
- Biodevices
- Quantum Dots
- Thermal Management Materials
- Optical Modulators

- Transistors
- Circuit Interconnects
- Single-molecule gas detection
- Solar Cells
- Desalination
- Ethanol Distillation
- Integrated Circuits
- T-Ray Scanners

1.3 Graphite Oxide (GO)

As a derivative of graphene, graphene oxide has also become an attractive material and been investigated widely in many areas since the ease of synthesizing graphene oxide and its solution processability[6]. Oxygen containing functional groups present on the surface are responsible for the hydrophilic properties of graphene. GO can be synthesized by the oxidative treatment of graphite by one of the principal methods [7-10] developed by

- Brodie
- Hummers
- Staudenmeir.

GO consists of graphene sheets with its surface decorated mostly with epoxide, carboxylic and hydroxyl groups [11]. Rapid heating of GO results in expansion and delamination, due to evaporation of the intercalated water and evolution of gases from pyrolysis of the oxygen containing functional groups. By its inherent nature, GO is electrically insulating. The presence of the oxygen containing functional groups makes Graphene Oxide thermally very unstable. It has been demonstrated that the electrical conductivity of GO (and presumably its thermal stability as

well) can be restored close to the level of graphite by chemical reduction using hydrazine hydrate. The structure and properties of graphite oxide depend on the synthesis method and the degree of oxidation.

CHAPTER 2

LITERATURE REVIEW

Stephen Wakeland et al [12] produced Graphene sheets from graphite oxide using a simple two-step process. Graphite oxide (GO) was homogeneously mixed with urea, an expansion–reduction agent, that decomposes upon heating to release reducing gases. The mix was heated in an inert atmosphere at 600^0 C. Graphene was readily collected as a by-product after cooling. Characterization of the samples were done by XRD, TEM, EELS, SEM, Raman Spectroscopy and the GO and urea mixtures decomposition-reduction process studied by TGA/DSC analysis. They proposed a mechanism in which urea had multiple functions in the process. First, urea creates volatile species that mechanically exfoliate the GO upon decomposition. Second, since these volatile species are reducing gases, they consequently remove most surface oxygen containing groups.

Stankovich et al [11] prepared graphene-based nano sheets by chemical reduction of graphite oxide via colloidal suspension route. GO used in this method was synthesized from natural graphite via Hummers method. GO was loaded in a round bottom flask in which water was added, which yielded an inhomogeneous yellow-brown dispersion. This dispersion was sonicated until it became clear with no visible particulate matter. Hydrazine hydrate was added as a reducing agent and the reaction was carried out in a reflux arrangement. Reduced GO precipitated out of the solution as a black mass. The precipitate was washed rigorously with water as well as methanol to remove all the residual acidic ions. Later it was dried on the funnel under a continuous air flow through the solid product cake. Different characterization techniques like SEM, Raman, XPS, NMR spectroscopy, TGA, elemental analysis and electrical conductivity were used to study the characteristics of the sample. Results indicated the formation of unsaturated and conjugated carbon atoms in the structure, which imparted electrical properties to the graphene sheets. Thus, he

concluded that reduced graphene oxide sheets may be used in hydrogen storage devices and as an electrically conductive filler material in composites.

Dohyung Kim et al [13] reported a simple, cost-effective, and environmental friendly process for reduction of graphite oxide by sulfuric acid treatment. The suggested process is a two-step reduction of graphite oxide, first in aqueous sulfuric acid medium at room temperature followed by reduction in concentrated sulfuric acid with refluxing.Various characterization techniques like XRD, XPS, Raman spectroscopy, thermal analysis demonstrated the quality of reduction of graphite oxide and was comparable in quality to the reduced graphite oxide synthesized using previously known methods that involve usage of toxic and hazardous reducing agents such as $NaBH_4$, hydrazine or hydrohalic acids.

Jincheng Liu et al [14] synthesized graphene, functionalized with oleylamine (OA) which was soluble in non-polar organic solvents, by combining the Hummers process for graphite oxidation, an amine-coupling process to prepare OA-functionalized graphite oxide (OA-GO), and a reduction process using trioctylphosphine (TOP). The role of TOP both a reducing agent and as an aggregation-prevention surfactant in the reduction of OA-GO was exploited in this reaction. Various characterization techniques like X-ray photoelectron spectroscopy, FTIR, XRD, TGA, and Raman spectroscopy confirmed the reduction of OA-GO. AFM confirmed the exfoliation of GO, OA-GO, and OA-functionalized graphene (OA-G). The conductivity of TOP-reduced OA-G showed that the reduction of functionalized GO by TOP is comparable to the reduction of GO by hydrazine.

Yenny Hernandez et al [15] demonstrated a novel method to exfoliate graphite which would give a suspension of graphene in water-surfactant solutions. The dispersion process was partially

optimised by optical characterisation of the graphene suspensions. Transmission electron microscopy showed the presence of small graphitic flakes in the dispersed phase. 40% of these flakes had less than 5 layers with 3% of flakes consisting of monolayers were observed. Coulomb repulsion due to the adsorbed surfactant was responsible for the stabilization of flakes in the suspension against reaggregation. However, it was observed that the larger flakes eventually settled down as sedimentation over 6 weeks, leaving only small flakes dispersed in the solution. Characterization techniques like Raman and IR spectroscopic analysis of these films suggested that the flakes were largely free of any defects and oxides. The study reported that the deposited films were reasonably conductive and were semi-transparent.

Daniela C. Marcano et al [16] reported an improved method for the preparation of graphene oxide (GO). Currently, the most common method for preparation of GO is Hummers' method. They excluded the $NaNO_3$, increased the amount of $KMnO_4$, and performed the whole reaction in a 9:1 mixture of H_2SO_4/H_3PO_4 improved the efficiency of the oxidation process. Greater amount of hydrophilic oxidized graphene material was reported as compared to Hummers' method. It was also reported that chemically converted graphene (CCG) produced from this new method was similar to the CCG produced by Hummer's method in its electrical conductivity. Unlike Hummers' method, this new method did not generate toxic gases and the temperature was easy to control. This study reported a method of improved synthesis of GO that may be important for large-scale production of GO and CCG.

Kaniyoor et al [17] investigated the properties of graphene prepared at low temperature by exfoliating graphitic oxide in reducing atmosphere, i.e. hydrogen atmosphere. GO was prepared by Modified Hummer's method using natural graphite. Graphite was properly mixed with NaCl and then washed properly with deionized water. The solution was filtered following which the

filtrate was stirred with conc. Sulphuric acid for 8 hours. It was followed by gradual addition of 6g of $KMnO_4$ maintaining the temperature below 20 °C. Constant stirring was done at 35 °C for 40 minutes and at 65 °C for 50 minutes. DI water was added to the solution prepared and it was heated to ~100 °C. The solution was further diluted by addition of 280 ml of water.30% H_2O_2 was added to the solution to further exfoliate the sheets. The obtained mixture was washed with 1:10 HCl, centrifuged and filtered. It was followed by washing continuously to increase the pH, and then vacuum drying was done to obtain the powders. The powder, thus produced, was characterized with XRD, FTIR, FESEM, Raman spectroscopy, BET, DSC, and XPS to study its properties.

Farman Ali et al [18] demonstrated that graphene can be formed via water soluble graphite oxide (GO), which can be reduced chemically or thermally to carbon. GO prepared via Hummer's method was shown to be EPR-active with ~1016 electron spins/g. On heating GO, the free radical concentration at ~140°C increased, followed by the elimination of CO_2 and H_2O, and finally producing black, diamagnetic graphitic material at high temperature. Thermal treatment leads to co-elimination of CO_2 and water and a large enhancement in transient free radicals, finally leading to EPR-inactive graphitic material. It appears possible that single sheets of GO deposited on mica substrates may be thermally converted to graphene-like molecule. Significant loss of carbon in the thermal process implies that the chemical route to graphene via Hummer's GO is less attractive.

Xiaobin Fan et al [19] reported that a stable graphene suspension resulted by simply heating an exfoliated-Graphene Oxide suspension under strongly alkaline conditions. NaOH was added to the GO suspension to improve the solubility of the alkyl free-radical initiator, but instead it was accompanied by a fast, unexpected color change (from yellow-brown to homogeneous black). Careful observations indicated that the exfoliated GO suspension had experienced fast

deoxygenation in presence of strongly alkaline solutions, resulting in stable graphene suspensions. This study reports that the interesting reaction can provide a green route to the synthesis of graphene with excellent dispersibility in water. Considering the nontoxicity and availability of sodium hydroxide, this study also opens an exciting opportunity for the production of graphene on an industrial scale.

Chen et al [20] investigated graphene oxide synthesized from expanded graphite in presence of a strong oxidant. Expanded graphite was put into concentrated sulphuric acid followed by gradual addition of $KMnO_4$ under constant stirring and cooling, maintaining the temperature of the mixture below 15 °C. Further stirring of the mixture was done at 35 °C for two hours with gradual addition of DI water. The reaction was terminated shortly after the addition of deionized water. Addition of 30% H_2O_2 solution (50 ml) caused violent which was accompanied by an increase of temperature to 100 °C and the change of color of the suspension changed to bright yellow. The suspension was later washed with HCl solution to remove the residual metallic ions. The paste collected from the filter paper after filtering was dried at 50 °C in an oven, until agglomerates were formed again. The agglomeration was dispersed in DI water for a couple of hours with constant stirring. The suspension was continuously washed with DI water for two days by filter paper and funnel, until the pH became 7. The brown paste, collected on the filter paper was dissolved in DI water and then ultrasonicated. Obtained dispersion was subjected to 30 minutes of centrifugation followed by dehydration in air at 60^0C. Various characterizations were performed on the samples to test the quality of the produced GO. This study highlights the approach to prepare large quantities of graphene oxide in industry via an inexpensive and simple method.

Mykola Seredych et al [21] synthesized Zirconium hydroxide/graphene composites from zirconium chloride and GO with the content of the graphene between 5-50%. The purpose of the

composite was to be used as adsorbents of sulphur dioxide. The starting and exhausted materials were characterized using adsorption of nitrogen, FTIR spectroscopy, potentiometric titration, SEM and thermal analysis. The results showed enhanced adsorption of SO_2 on the composites. This phenomenon was explained by the formation of new basic sites and porosity as a result of interactions between the oxygen groups attached to the graphene layers and zirconium hydroxide matrix.

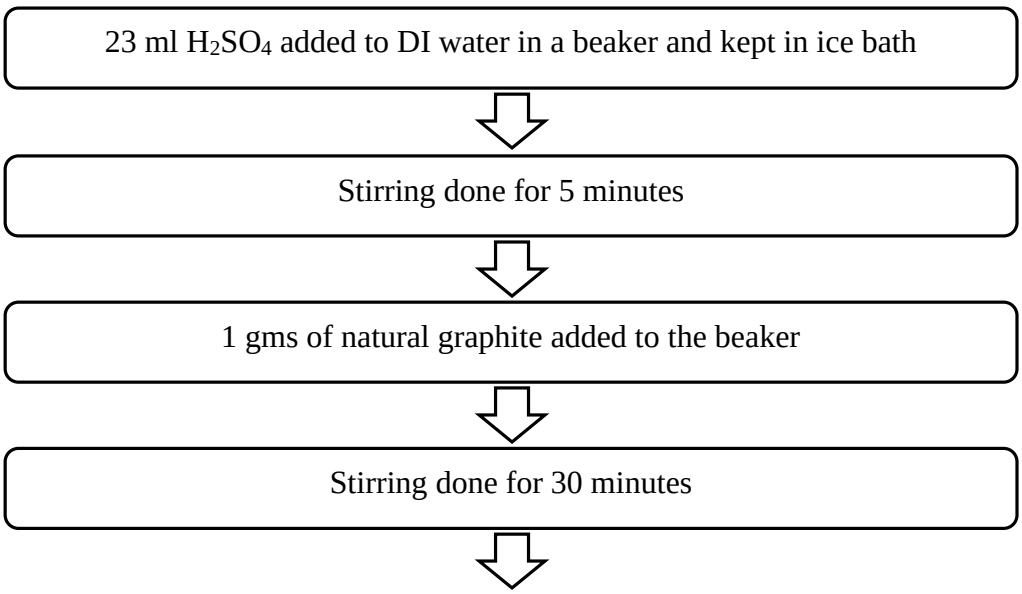
CHAPTER 3

EXPERIMENTAL

3. Experimental

3.1 Synthesis of Graphene Oxide by Modified Hummer's Method (Method - 1)

Graphene Oxide was synthesized by oxidizing and exfoliating natural graphite by Modified Hummer's method [20]. The whole method has been briefly shown in fig. 2. 23 ml of H_2SO_4 was taken in a beaker and kept inside an ice bath (Temperature ~ 0 ^oC). Stirring was done for 5 minutes. 1 gram of natural graphite (99% pure) obtained from "Loba Chemie" was added to the beaker under constant stirring for 30 minutes to ensure proper dispersion in the liquid medium. 3 grams of $KMnO_4$ was added while maintaining the temperature of the beaker under 20 ^oC with constant stirring for 30 minutes. The beaker was transferred to a water bath where the temperature was slowly raised to 35 ^oC. 46 ml of DI water was added slowly to the solution over a period of 2 hours. The mass initially gets converted from red oil to a black colored solution. The solution was further diluted with the addition of the remaining 140 ml of DI water. Temperature of the solution was further raised to 100 ^oC. The solution was heated for 1 hour. 2.5 ml of 30% H_2O_2 was added to the solution and was allowed to cool overnight.



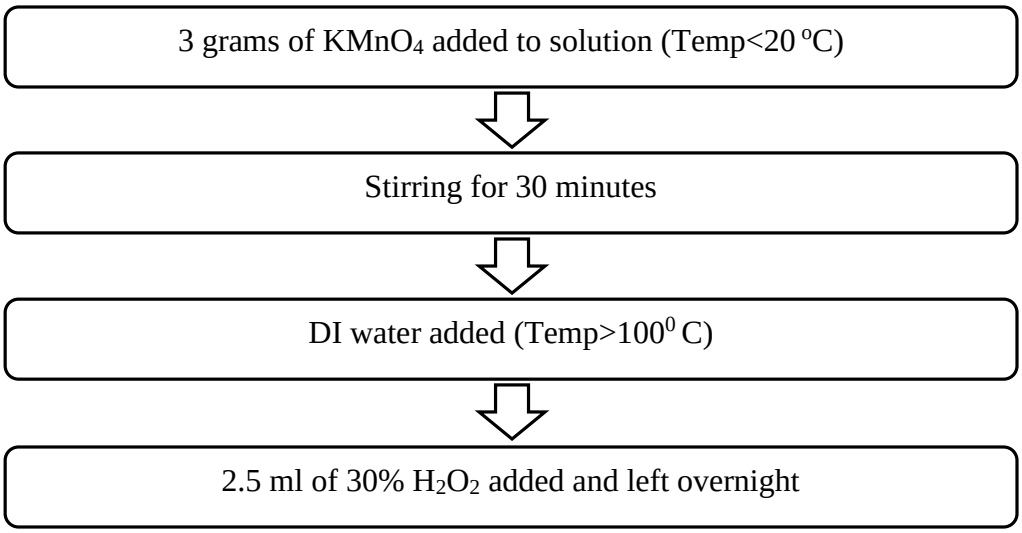


Fig. 2 Flowchart for synthesis of Graphene Oxide by Modified Hummer's Method

3.2 Synthesis of Graphene Oxide by Modified Hummer's Method (Method - 2)

Graphene Oxide was again tried to synthesize by oxidizing and exfoliating natural graphite by Modified Hummer's method [20] but with a slight modification this time. The entire procedure has been concisely mentioned in Fig. 3. 23 ml of H_2SO_4 and 0.5 grams $NaNO_3$ was taken in a beaker and put inside an ice bath (Temperature ~ 0^o C). Stirring was done for about 15 minutes. 1 gram of natural graphite (99% pure) obtained from "Loba Chemie" was added to the beaker under constant stirring for 30 minutes. 3 grams of $KMnO_4$ was added while maintaining the temperature of the beaker under 20 °C at the same time with constant stirring for 30 minutes. The solution turned into a thick black paste. The beaker was then transferred to a water bath where the temperature was slowly raised to 35 °C. 46 ml of DI water was added slowly to the solution over a period of 2 hours. The mass initially gets converted from red oil to dark green color. Temperature of the solution was

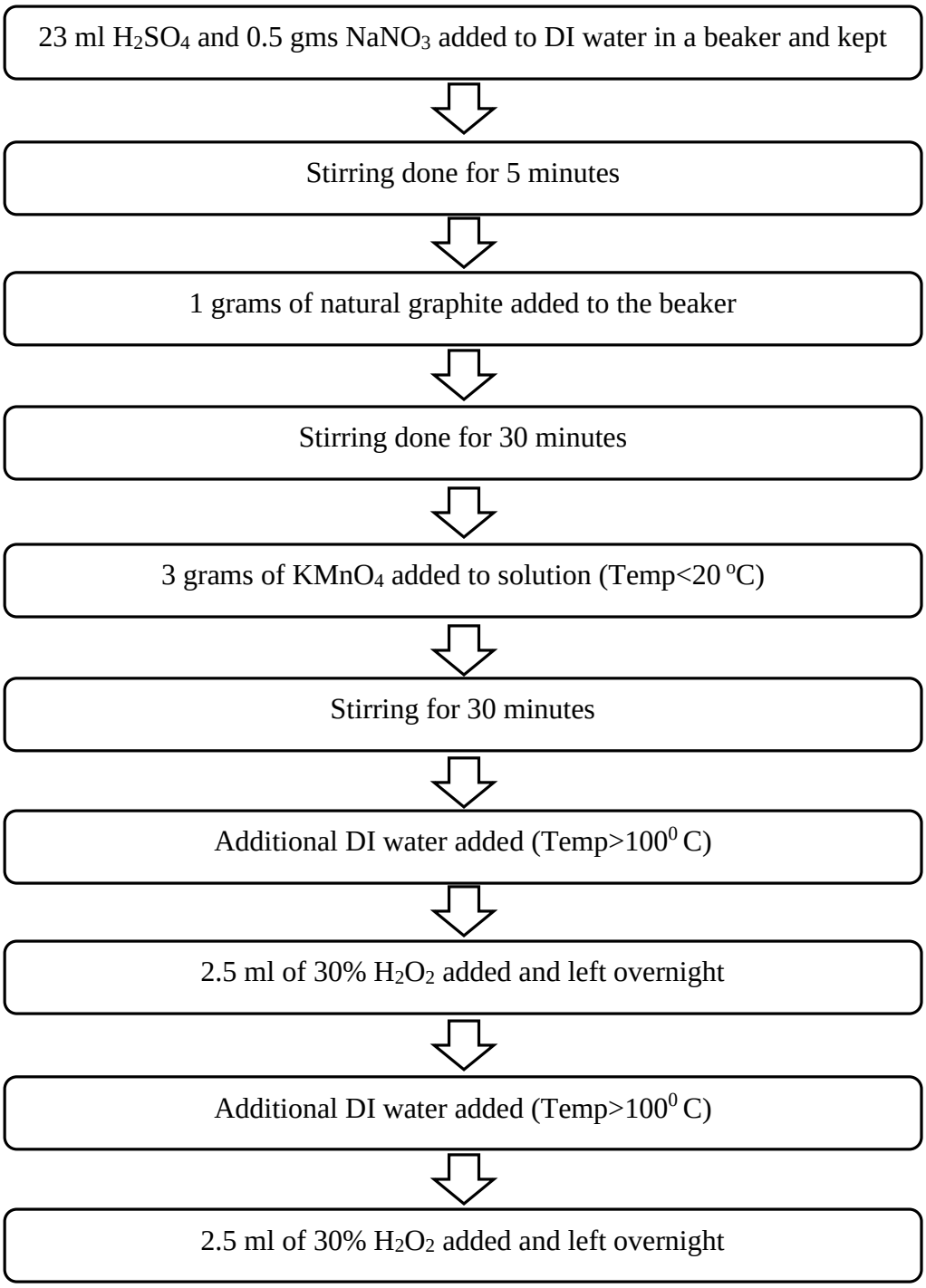


Fig. 3 Flowchart for synthesis of Graphene Oxide by Modified Hummer's Method

raised to 100 ^{o}C with the addition of the remaining 140 ml of DI water. The color of the solution changed to yellowish green. The solution was further heated for 1 hour. 2.5 ml of 30% H_2O_2 was added to the solution and was allowed to cool overnight with constant stirring to allow complete exfoliation.

3.3 Stabilization of Graphene Oxide suspension

Due to the usage of concentrated H_2SO_4 by Modified Hummer's method, the prepared GO was very acidic. The prepared GO solution was first washed with 250 ml of [1:10 HCl] and then collected on a filter paper of mesh size 40. The GO suspension was unstable owing to the presence of residual metal ions which resulted in the agglomeration or partial exfoliation of the graphene oxide sheets. Thus an attempt was made to stabilize the solution by washing the solution repeatedly with DI water thus increasing its pH. Zeta potential being a function of pH being directly proportional to it, increases with increase in pH.

Washing of the Graphene Oxide prepared by Modified Hummer's method

The whole washing phase of the experiment was repeated keeping the concentration of the solution nearly same throughout the study. Fig. 3 describes the process of washing in which the concentration is kept constant. The washing procedure has been shown stepwise in fig. 4. 0.1 gms of dried graphene oxide were taken and added to 200 ml of DI water to make a dilute solution. The solution was washed in an arrangement using filter paper of mesh size 40. The residue was

washed with DI water and collected in a crystallizer to make a solution of 200 ml and the whole process was repeated till the solution reached a pH of 7. After each wash, small amounts of the solution were taken in a vial and individual pH were recorded. The vials containing solution at different pH were used for UV-vis, FTIR and DLS-particle size analyzer study.

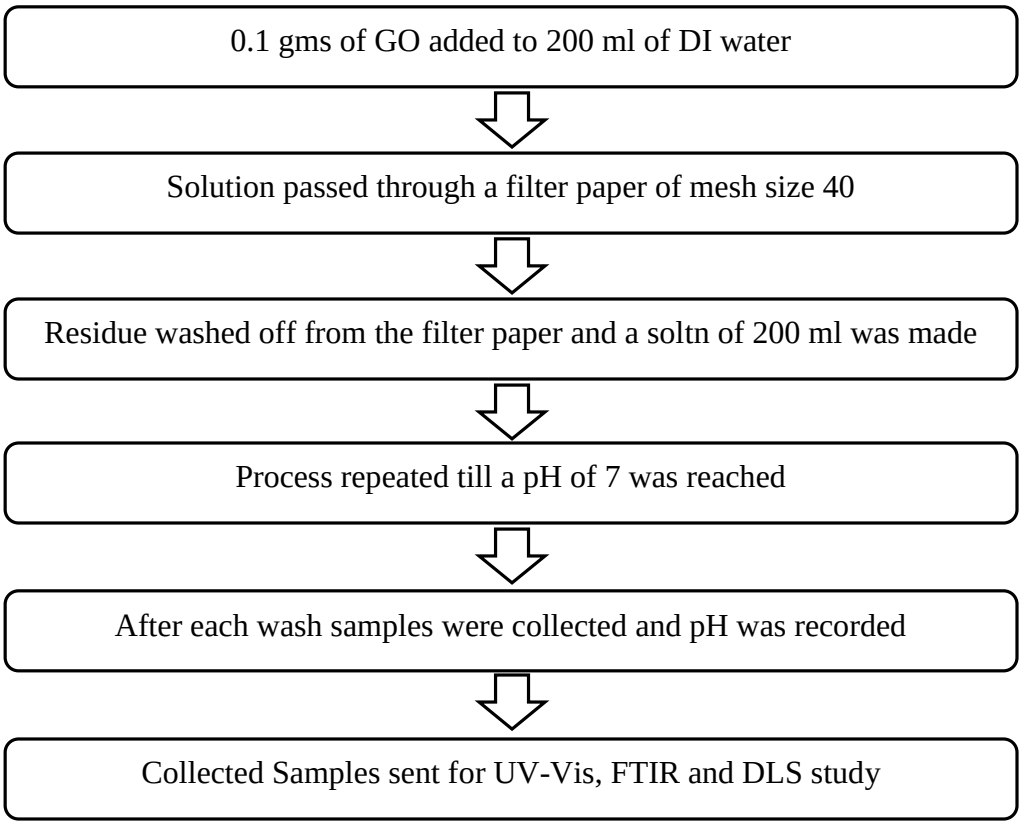


Fig. 4 Flowchart for washing of GO solution

After a pH of 7 was reached and the suspension had fully stabilized, the residue in the filter paper after filtering was washed off and collected in a crystallizer. The solution was then kept in an oven at 50 ^{o}C for overnight drying.

3.4 Reduction of Graphene Oxide (GO) to Chemically Converted Graphene Oxide (CCG)[22]

0.5 ml of GO solution (0.5 mg/ml) was mixed with 5 ml DI water in a 20 ml vial. Ultra sonication was done for 15 minutes to ensure proper dispersion of the solution. Stirring was done for 30 minutes. 5 µl N_2H_2 (35 % in water) and 35 µl of NH_3 (28% in water) was added to the solution. Vigorous stirring was done for several minutes to ensure proper mixing and homogenization of the solution. The vial was then kept in a water bath and treated isothermally in a reflux system (Temperature ~ 95 ^oC) for about 1 hour. The solution was then transferred to a petri dish which was then dried in an oven at 50 ^oC for several hours. Fig. 5 shows the flowchart of the process to prepare chemically converted graphene.

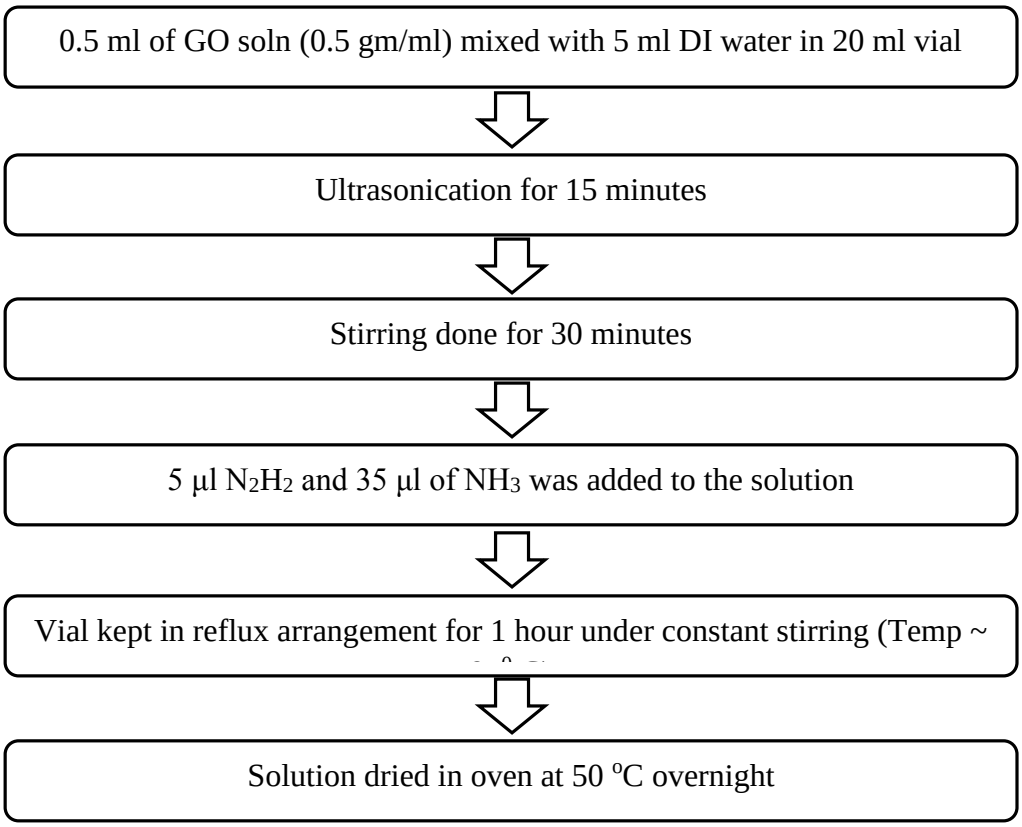


Fig. 5 Preparation of CCG by isothermal treatment in Reflux arrangement

3.5 Synthesis of Few Layer Graphene – Zirconia composite

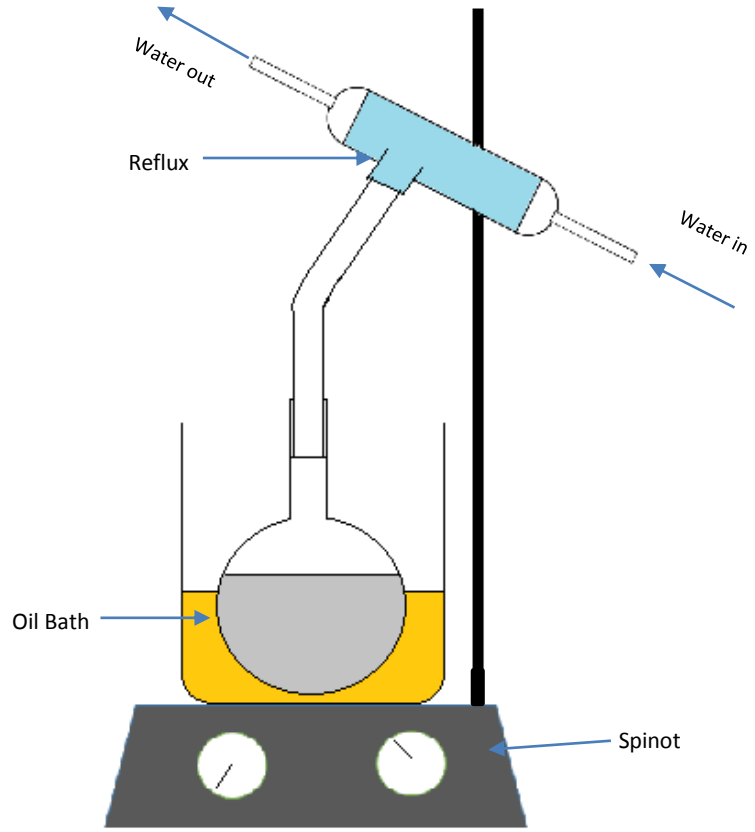


Fig. 6 Schematic of the reflux arrangement

$ZrOCl_2.8H_2O$ was used a precursor to prepare the zirconia matrix in which graphene sheets were to be incorporated. 20 gms of $ZrOCl_2.8H_2O$ were taken in an agate mortar and crushed till very fine powder was achieved. The powder was then dried in vacuum oven for 2 hours. 0.02 grams of CCG was added to 100 ml of DI water in a beaker. The solution was ultrasonicated for 30 minutes in a Longhorn Sonicator to ensure proper dispersion and homogenization of CCG in DI water. The solution turned into black color. 6.445 grams of $ZrOCl_2.8H_2O$ was added to the solution under constant stirring on a spinot. Stirring was done for another 30 minutes. The beaker was then transferred to a reflux arrangement. 2 grams of NaOH was added to the solution following which the solution was isothermally treated in a reflux system as shown in fig. 6 for 72 hours at (90-120 ^oC) under constant stirring. During the reaction, ultrasonication was done using Longhorn Sonicator for 45 minutes in an interval of 24 hours to ensure proper mixing and dispersion of the graphene sheets. Temperature was constantly monitored throughout the reaction to ensure that the temperature does not exceed beyond 120 ^oC. After the reaction was over, the solution was cooled and washed with

hot water. The precipitate was collected by centrifugation and washed with hot water several times to remove the ions present in it. The precipitate was collected in a petri dish and oven dried overnight. The precipitate after drying formed thread like structures. Fig. 7 describes the whole method stepwise.

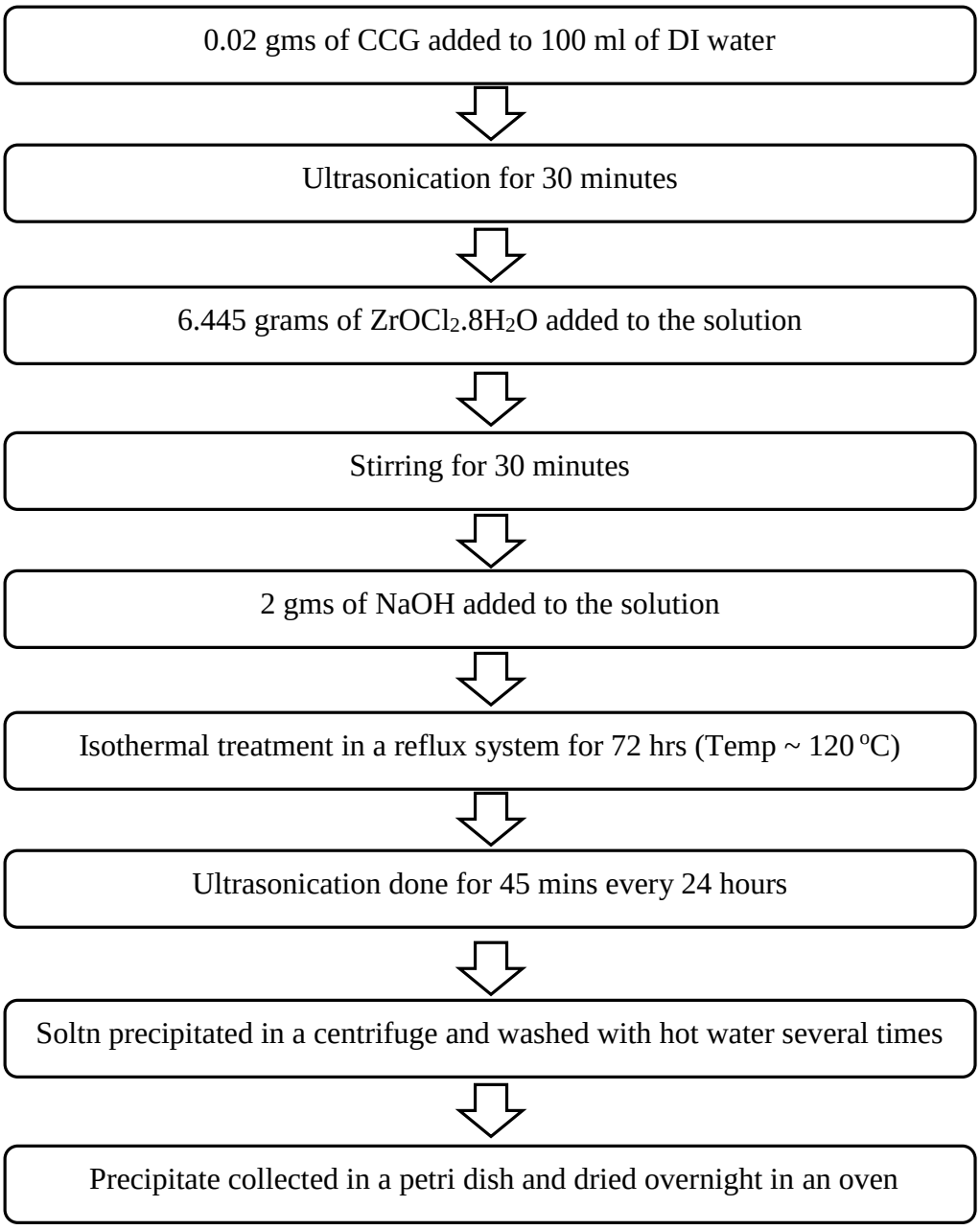


Fig. 7 Synthesis of FLG-ZrO_2 composite

3.6 Calcination

Calcination of the dried fibres was carried out in a reducing atmosphere to avoid oxidation of graphene to carbon dioxide at varying temperatures; one at 600^{o}C and other at 800^{o}C. For each sample calcined at a particular temperature, characterization techniques were employed to study the formation of crystalline zirconia in the composite fibres.

3.7 Characterization Techniques

3.7.1 X-Ray Diffraction

X-ray powder diffraction (XRD) is an analytical technique primarily used for phase identification of a crystalline material, crystal structure and getting information on unit cell dimensions and atomic spacing. The working of X-ray diffraction is based on constructive interference of monochromatic X-rays and the crystalline sample. X-rays are generated by a cathode ray tube which are directed towards the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$).

Where, d = spacing between diffracting planes,

θ = incident angle,

n = order of diffraction

λ = wavelength of the beam

The samples were glued to a glass slide and XRD analysis was performed by Philips' X-ray diffractometer with Nickel filtered Cu Kα radiation (1.5406 Å). The diffraction was done at angle 10°-60º with scanning speed 2º per min.

3.7.2 UV-Visible Spectroscopy

Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. It uses light in the ultraviolet and adjacent visible ranges. The absorption or reflectance in the visible range directly affects the color of the chemicals. Molecules undergo electronic transitions in this region of electromagnetic spectrum. Many molecules absorb ultraviolet or visible light.

Beer Lambert's Law states that:

$A = \varepsilon bc$,

where 'ε' is a constant called the absorbtivity, b is the path length and c is the concentration of the adsorbing species. Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the Highest Occupied Molecular Orbitals and the Lowest Unoccupied Molecular Orbitals), the longer the wavelength of light it can absorb.

3.7.3 Thermal Analysis

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis which measures changes in physical and chemical properties of materials as a function of temperature at a constant heating rate, or as a function of time. It can provide information about physical phenomena such as second-order phase transitions, including absorption, vaporization, desorption, sublimation and adsorption. TGA can also provide information about the chemical phenomena including desolvation (especially dehydration), decomposition, chemisorptions, and solid-gas reactions.

3.7.4 FTIR Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, photoconductivity, emission or Raman scattering of a liquid, solid or gas. An FTIR spectrometer collects spectral data for a wide range of wavelengths. In this technique, a beam consisting of a wide range of frequencies of light is directed to the sample and the amount of beam absorbed by the sample is measured. Next, the beam is modified to contain a different combination of frequencies which give a second data point. This process is repeated several times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength. FTIR spectroscopy of GO samples at different pH in liquid medium was done to study the presence of different functional groups in it.

3.7.5 Scanning Electron Microscopy

A scanning electron microscope (SEM) is a type of electron microscope that produces images of solid specimens by scanning its surface with a beam of high energy electrons that are focused onto the sample. The electrons interact with the sample, producing various detectable signals that contain information about the sample's external morphology (texture), chemical composition, and crystalline structure and orientation of materials. The types of signals produced by a SEM include back-scattered electrons (BSE), secondary electrons (SE), light (cathodoluminescence) (CL), characteristic X-rays, specimen current and transmitted electrons. Nonconductive specimens have the tendency to accumulate charge when scanned by the electron beam which causes errors in scanning. To avoid this, surfaces of samples are usually coated with an ultrathin coating of electrically conducting material. Zirconia – CCG samples were coated with platinum in a low-vacuum sputtering unit and microstructural analysis was done using JEOL-JSM 6480LV SEM.

CHAPTER 4

RESULTS AND DISCUSSIONS

4 Results and Discussions:

4.1 XRD

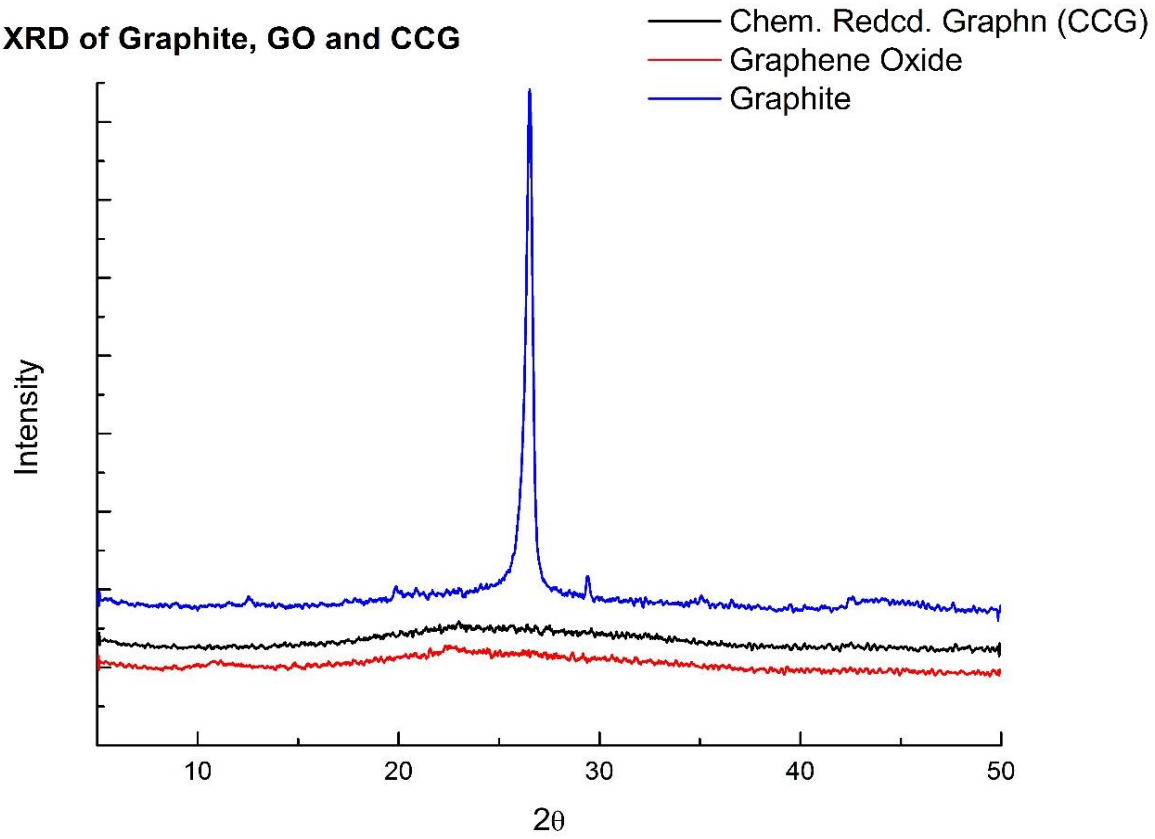


Fig. 8 X-Ray diffraction of pure graphite, graphene oxide and chemically converted graphene

Fig. 8 represents XRD diffraction patterns of graphite, chemically converted graphene and graphene oxide respectively. Graphene has a characteristic sharp peak at $2\theta = 26.5^{o}$ which transforms into a broad peak with no intense or distinct peaks for graphene oxide. In some literature it may be found that XRD diffraction pattern for graphene oxide shows a peak for $2\theta=11.26^{o}$ which corresponds to the exfoliation of graphene sheets to about 8-10 Å from the usual 3 Å. However, in this case it exhibits complete exfoliation of the layers indicating that no order is observed within

the layers. Oxidation of graphite by strong oxidising agents like $KMnO_4$ and H_2O_2 results in the formation of few sheets like structure of graphene oxide with corrugated structure. Further exfoliation on increasing the pH value of the suspension results in vanishing of the regular periodicity of graphite. This explains the absence of any sharp peaks in the XRD of GO. Reduction of GO results in CCG where functional groups are absent but the periodicity is absent due to corrugated, exfoliated few layer sheets.

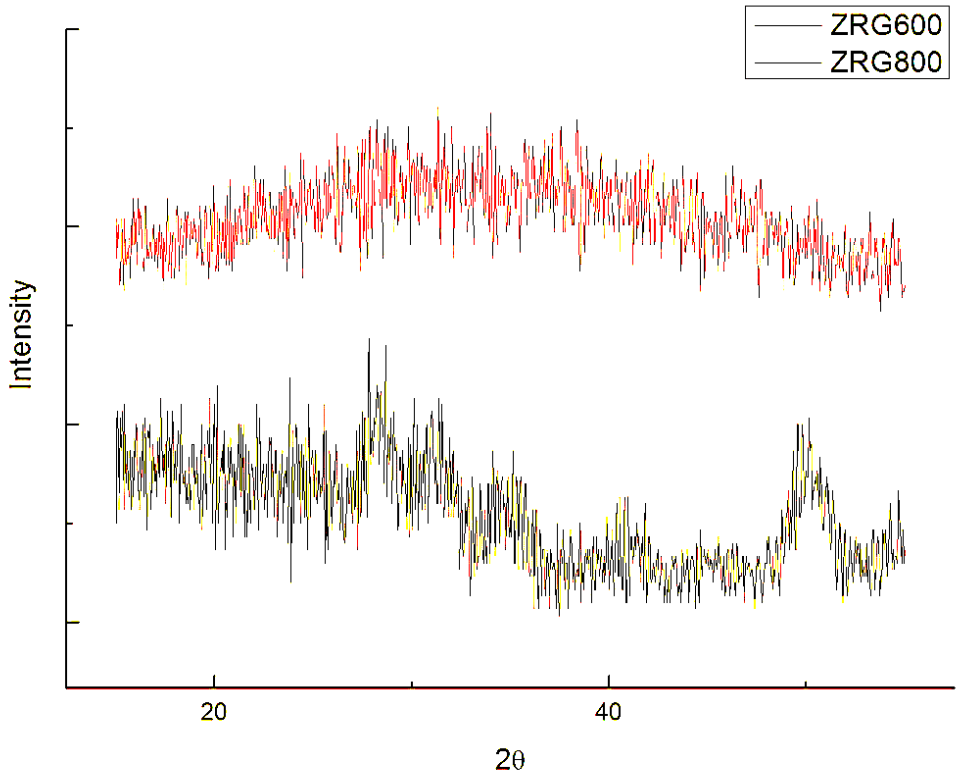


Fig. 9 X-Ray diffraction of FLG-zirconia composite calcined at 600 ^oC and 800 ^oC

Fig. 9 represents the XRD diffraction pattern of zirconia-CCG composites calcined at 600 ^oC and 800 ^oC respectively. The composites calcined at 600 ^oC have a broad peak suggesting the presence of amorphous zirconia whereas the XRD pattern for composites calcined at 800 ^oC show partial

crystallization to m-zirconia indicated by the peaks for 2θ = 28.21° and 31.45° and partially to t-zirconia indicated by peaks for 2θ = 35.40° and 50.70°

4.2 Uv-Vis Spectroscopy

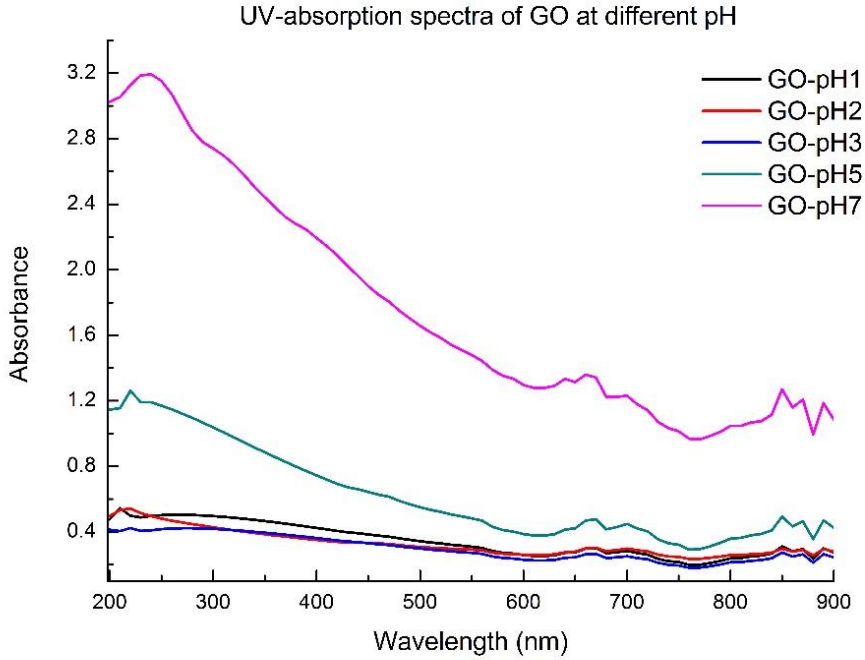


Fig. 10 UV-Vis spectroscopy of GO samples with increasing pH value.

As shown in Figure 10, the maximum absorption peak of Graphene Oxide at 230 nm for each sample indicates that the maximum adsorption peak is independent of the pH of the solution. It can also be concluded that with increase in pH, there is gradual increase in the adsorbance of the light passing through the solution. It can be explained on the basis of Beer-Lambert's law where adsorbance is directly proportional to the number of adsorbants. With increase in pH, the residual acidic ions are washed off the solution which results in the intercalation of water into the graphene sheets, thus further exfoliating and separating the sheets. With the separation and dispersion of

sheets in the dispersing medium, the number of adsorbants rapidly increases which results in the increase in adsorbance value.

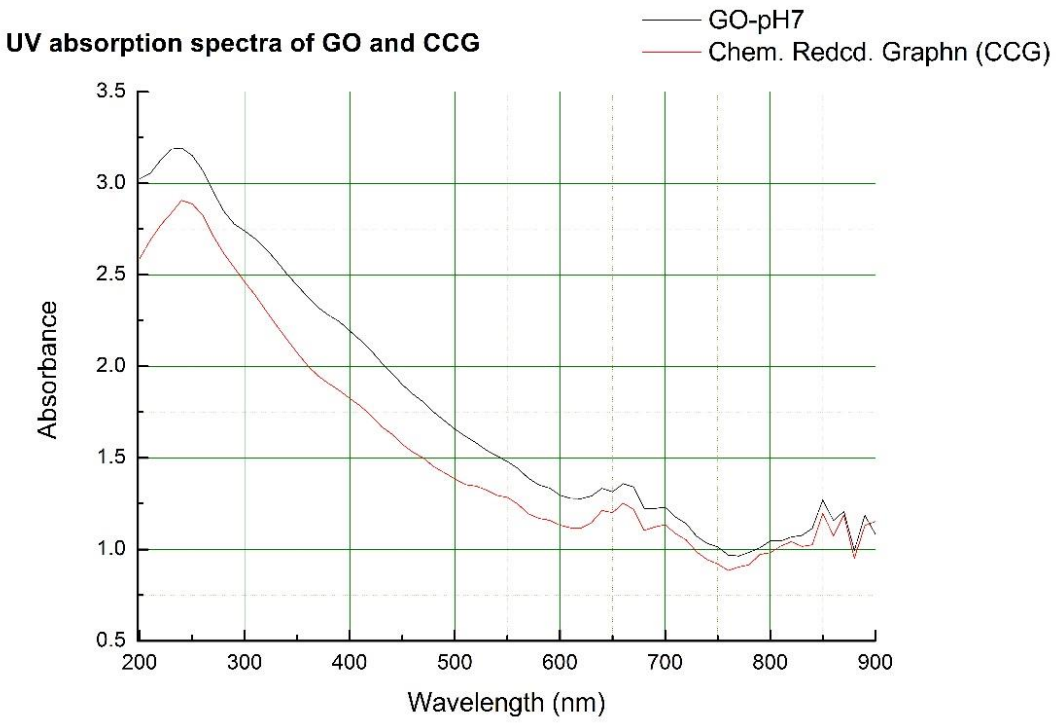


Fig. 11 UV-Vis spectroscopy of graphene oxide at pH 7 and chemically converted graphene

As shown in Figure 11, the maximum absorption peak of Graphene Oxide at 230 nm corresponding to π-π^* transition of aromatic C-C bonds red-shifted to 255 nm for Chemically Converted Graphene, indicating that the electronic conjugation within the reduced graphene sheets was revived upon partial reduction of graphene oxide. This phenomenon of red shift has been used as a monitoring tool for the reduction of GO[23].

.

4.3 Thermal Analysis

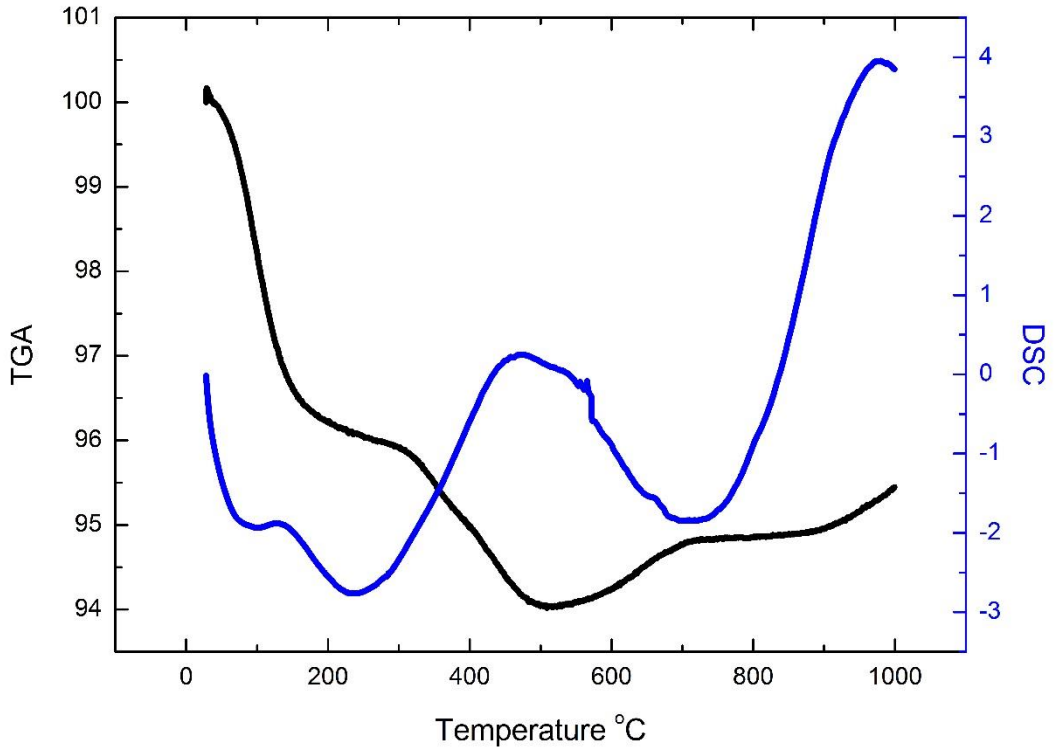


Fig. 12 Thermal analysis of FLG-zirconia composite

As shown in fig. 12, initially, with increase in temperature, adsorbed water/moisture present in the composite goes off which involves a certain percentage of mass. After dehydration, the zirconium hydroxide readily decomposes into amorphous zirconia due to dehydroxylation with increasing temperature which appears as a sharp exothermic peak around 460 ^{o}C [24]. On heating further, another exothermic peak, i.e. peak for crystallization temperature comes around 900 ^{o}C where the amorphous zirconia crystallizes to a crystalline phase of zirconia.

4.4 FTIR Spectroscopy

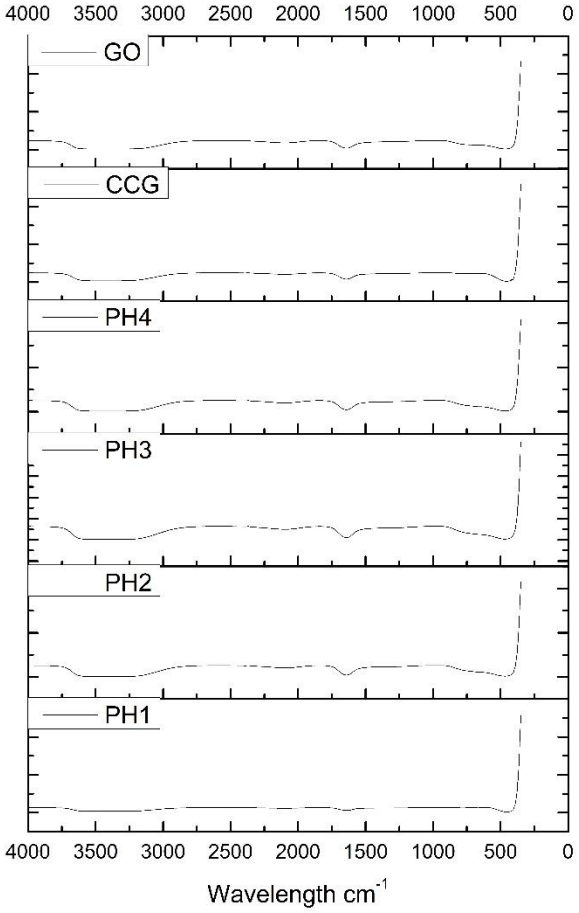


Fig. 13 FTIR-spectroscopy for GO with varying pH and CCG

Fig. 13 shows FTIR spectra of graphene oxide at different pH and chemically converted graphene. The presence of different type of oxygen containing functional groups in graphene oxide was confirmed at 3400 cm^{-1} (O-H stretching vibrations), at 1720 cm^{-1} (stretching vibrations from C=O), at 1220 cm^{-1} (C-OH stretching vibrations), and at 1060 cm^{-1} (C-O stretching vibrations)[25]. As there is no significant in the peak intensity of GO at different pH and CCG, nothing substantial can be concluded from the FTIR characterization about the conversion of graphene oxide to CCG.

4.5 SEM (Microstructural Analysis)

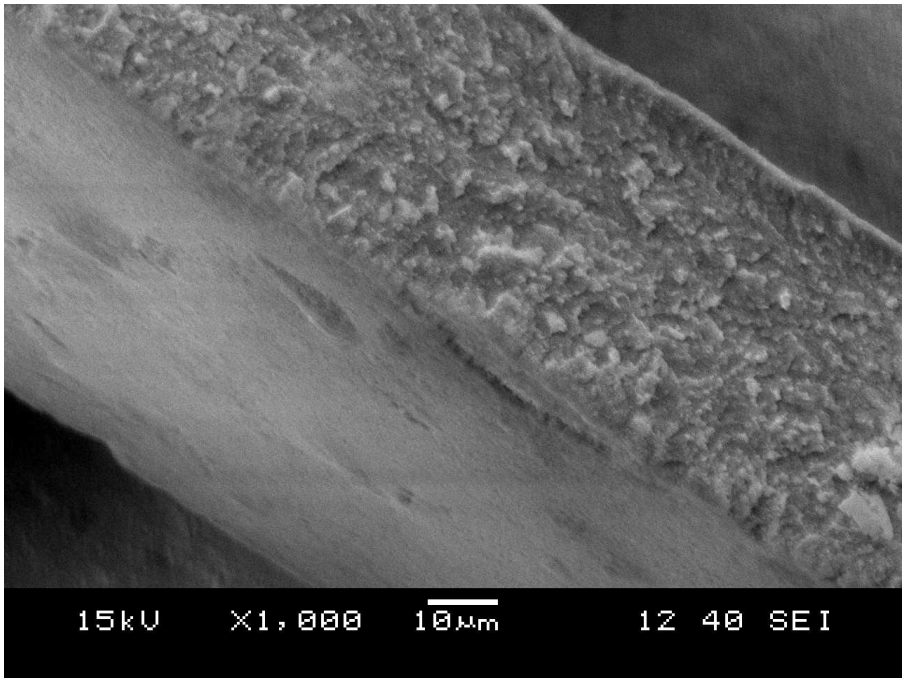


Fig. 14.a SEM micrograph of FLG-zirconia composite calcined at 600^0 C

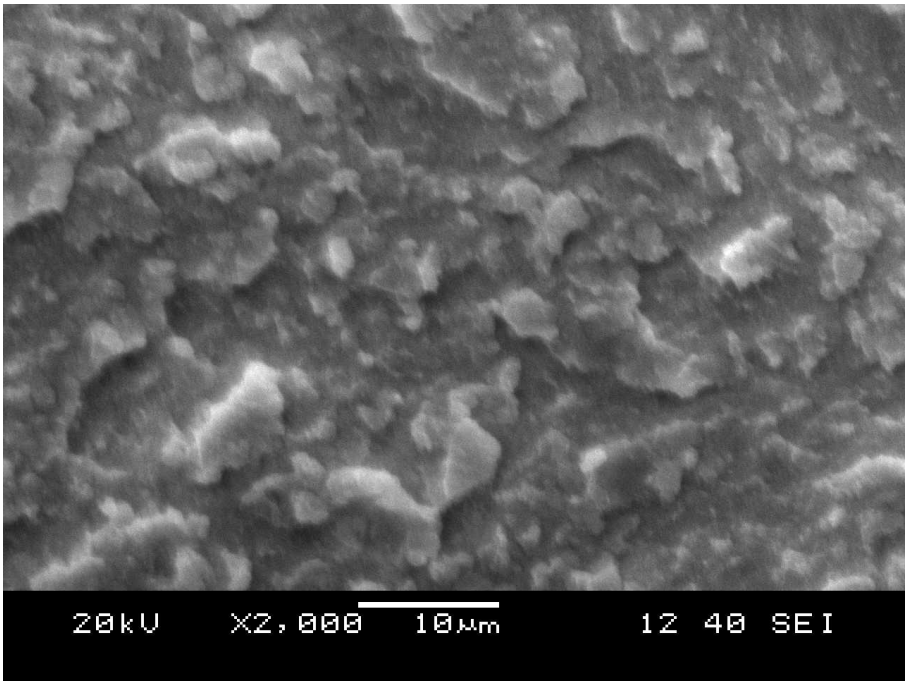


Fig. 14.b SEM micrograph of FLG-zirconia composite calcined at 600^0 C

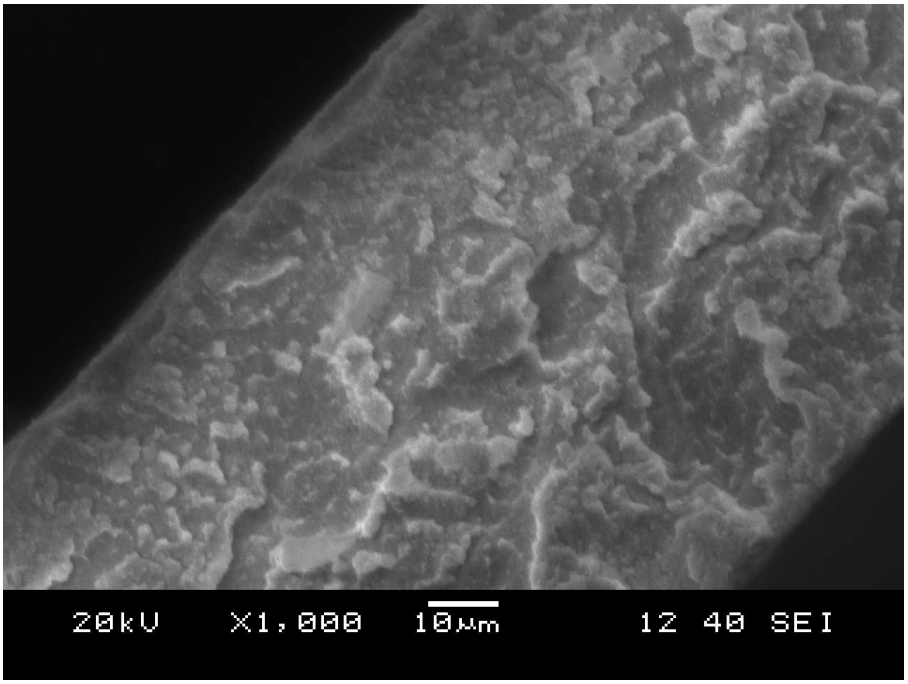


Fig. 15.a SEM micrograph of FLG-zirconia composite calcined at 800^0 C

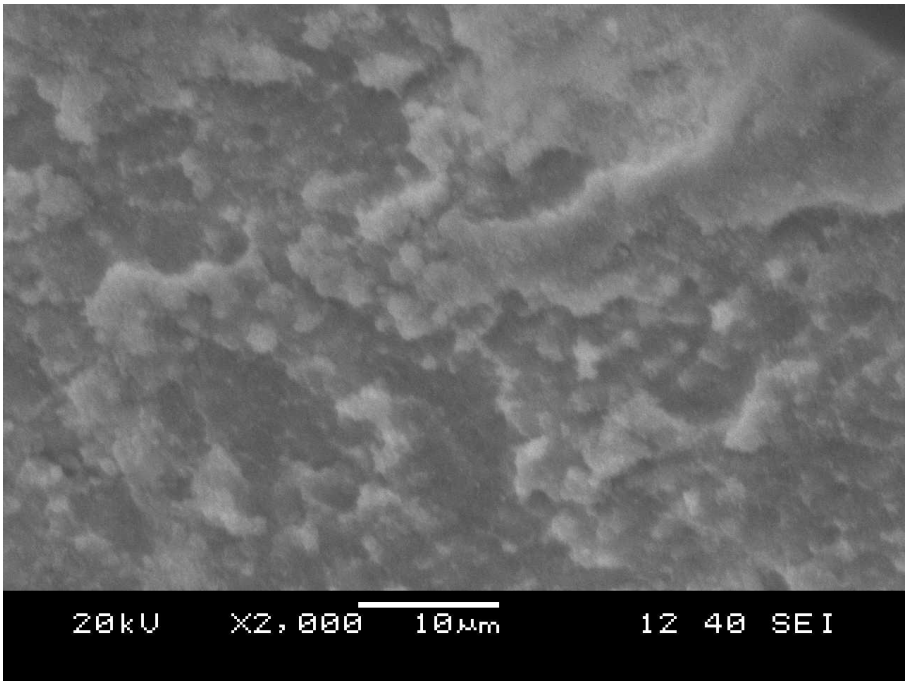


Fig. 15.b SEM micrograph of FLG-zirconia composite calcined at 800^0 C

SEM micrograph of the As-synthesised powders calcined at 600 ^oC are shown in fig 14.a and 14.b. SEM micrograph of the powders calcined at 800 ^oC are shown in fig. 15.a and 15.b

CHAPTER 5

CONCLUSIONS

5. Conclusions:

1. Water dispersible graphene oxide was synthesized and it was found that pH had a major role to play in its dispersability in a polar solvent, e.g. water

2. CCG was fabricated by reduction of graphene oxide. CCG, unlike graphene, is water dispersible (hydrophilic). Due to partial reduction, oxygen containing functional groups (-COOH, -OH, >O) are still present on the edges as well as on the basal plane.

3. The red shift associated with the formation of CCG from GO may be due to the excited orbital states of CCG.

4. FLG/ZrO_2 composites were synthesized by isothermal reflux method. XRD of as-synthesised powders were calcined at 600 ^oC showed amorphous character. XRD of powders calcined at 800 ^oC showed partial crystallization with the small peaks at positions corresponding to 100% m-ZrO_2 and 100% t-ZrO_2.

5. Crystallization of amorphous zirconia may have been delayed to 900^oC due to incorporation of graphene in the matrix.

References

[1] K. Novoselov et al : Electric field effect in Atomically Thin Carbon films : *Science 306 [666-669] (2004)*

[2] Y. Zhu , S. Murali , W. Cai , X. Li , J.W Suk, J.R. Potts, R.S. Ruoff : Graphene and Graphene Oxide : Synthesis, Properties, and Applications: *Advanced Materials 22 [3906–3924] (2010)*

[3] Q. Liu, J. Shi, M. Cheng, G. Li, D. Cao, G. Jiang : Preparation of graphene-encapsulated magnetic microspheres for protein/peptide enrichment and MALDI-TOF MS analysis : *Chemical Communications 48 [1874-1876] (2012)*

[4] H. Suna, Y. Yangb, Q. Huang: Preparation and Structural Variation of Graphite Oxide and Graphene Oxide : *Integrated Ferroelectrics 128 [163-170] (2011)*

[5] Z. Xu, C. Gao : Graphene chiral liquid crystals and macroscopic assembled fibres : *Nature Communications 571 (2011)*

[6] Xuebing Hu, Yun Yu , Weimin Hou, Jianer Zhou, Lixin Song: Effects of particle size and pH value on the hydrophilicity of graphene oxide, *Applied Surface Science 273 (2013) 118– 121*

[7] S. Mao, H. Pu, J. Chen : Graphene oxide and its reduction: modeling and experimental progress : *RSC Adv. 2 [2643-2662] (2012)*

[8] B.C. Brodie: Sur le poids atomique du graphite: *Ann. Chim. Phys. 59 [466–472] (1860)*

[9] W. Hummers, R. Offeman: Preparation of graphitic oxide : *Journal of the American Chemical Society 80 [1339] (1958)*

[10] J.H. Chen, C. Jang, S. Xiao, M. Ishigami, M.S. Fuhrer: Intrinsic and extrinsic performance limits of graphene devices on SiO_2: *Nature Nanotechnology 3 [206-209] (2008)*

[11] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhamme, Y. Jia, Y. Wu, S.T.Nguyen, R.S. Ruoff : Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide : *Carbon 45 [1558–1565] (2007)*

[12] Stephen Wakeland, Ricardo Martinez, John K. Grey, Claudia C. Luhrs: Production of graphene from graphite oxide using urea as expansion–reduction agent, *CARBON 48 (2010) 3463–3470*

[13] Dohyung Kim, Seung Jae Yang, Yern Seung Kim, Haesol Jung, Chong Rae Park: Simple and cost-effective reduction of graphite oxide by sulfuric acid, *Volume 50, Issue 9, August 2012, Pages 3229–3232*

[14] Jincheng Liu, Huiseong Jeong, Jinzhang Liu, Kyungmoon Lee, Ji-Yong Park,Y.H. Ahn, Soonil Lee: Reduction of functionalized graphite oxides by trioctylphosphine in non-polar organic solvents, *CARBON 48 (2010)* 2282 –2289

[15] Y. Hernandez, M. Lotya, V. Nicolosi, F.M.Blighe, S. De, G. Duesberg, J.N.Coleman: Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions: *Journal of American Chemical Society 131 [3611-3620] (2009)*

[16] D.C. Marcano et al: Improved synthesis of graphene oxide: *Journal of the American Chemical Society 4 [4806-4814] (2010)*

[17] A. Kaniyoor, T.T. Baby, S. Ramaprabhu: Graphene synthesis via hydrogen induced low temperature exfoliation of graphitic oxide: *Journal of Materials Chemistry 20 [8467-8469] (2010)*

[18] Farman Ali, Neeraj Agarwal, Pabitra K. Nayak, Ranjan Das and N. Periasamy: Chemical route to the formation of graphene ,*CURRENT SCIENCE, VOL. 97, NO. 5, 10 SEPTEMBER 2009*

[19] Xiaobin Fan, Wenchao Peng, Yang Li, Xianyu Li, Shulan Wang, Guoliang Zhang, and Fengbao Zhang: Deoxygenation of Exfoliated Graphite Oxide under Alkaline Conditions: A Green Route to Graphene Preparation, *Adv. Mater. 2008, 20, 4490–4493*

[20] J.H. Chen, C. Jang, S. Xiao, M. Ishigami, M.S. Fuhrer: Intrinsic and extrinsic performance limits of graphene devices on SiO_2 : *Nature Nanotechnology 3 [206-209] (2008)*

[21] Mykola Seredych and Teresa J. Bandosz: Effects of Surface Features on Adsorption of SO_2 on Graphite Oxide/$Zr(OH)_4$ Composites, *J. Phys. Chem. C 2010, 114, 14552–14560*

[22] Yuxi Xu, Kaixuan Sheng, Chun Li and Gaoquan Shi: Highly conductive chemically converted graphene prepared from mildlyoxidized graphene oxide: *J. Mater. Chem., 2011, 21, 7376*

[23] Li, D. et al., *Nature Nanotechnol. 2008, 3, 101*

[24] Gong-Yi Guo,Yu-Li Chen, Wei-Jiang Ying, Thermal, spectroscopic and X-ray diffractional analyses of zirconium hydroxides precipitated at low pH values, *Materials Chemistry and Physics 84 (2004) 308–314*

[25] Xu, Y. et al, *J. Am. Chem. Soc. 2008, 130, 5856*